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(21) International Application Number: PCT/US92/01974 (22) International Filing Date: 12 March 1992 (12.03.92) (30) Priority data: 701,119 16 May 1991 (16.05.91) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: WU, Kam, C. ; WEIGL, Stefan ; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: JORDAN, Robert, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: EPOXIDE-BASED ADHESIVE (57) Abstract Photopolymerizable epoxide-based adhesives that are tacky and pressure-sensitive at room temperature and that provide high increased bond strength when cured. Also, transparent overlays comprising protective cover sheets and a layer of such adhesives.		

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EPOXIDE-BASED ADHESIVEField of Invention

5 The present invention relates to epoxide-based adhesives, particularly adhesives whose bond strength is enhanced through photopolymerization. The invention also relates to transparent overlays with such adhesive which can be applied to documents to deter tampering.

10

Background

 Pressure-sensitive adhesives ("PSAs") exhibiting tackiness at room temperature have been made in a variety of compositions. Such adhesives offer
15 advantages of easy application, with successful bonding typically being achieved upon application of limited pressure, e.g., hand pressure. In many cases, such adhesives tend to exhibit reduced bond strength when subjected to elevated temperatures or organic solvents.

20

 Although the bond strength of pressure-sensitive adhesives is acceptable for many applications, in some instances, an adhesive that provides useful room temperature tackiness as well as resistance to adhesive failure under elevated
25 temperatures or upon exposure to organic solvents is desired.

 One technique sometimes used to improve the performance, e.g., increase the shear strength and peel resistance, of certain pressure-sensitive adhesives at
30 elevated temperatures or in the presence of organic solvents is to further crosslink the adhesive after its application to a substrate. Such crosslinking can be induced photochemically or thermally, or via chemical reaction, e.g., such as with moisture or encapsulated
35 reactants. It has been observed, however, that in some instances crosslinking a pressure-sensitive adhesive results in a reduction in adhesiveness. For example, U.S. Patent No. 4,286,047 (Bennett et al.) discloses a normally tacky, pressure-sensitive adhesive having an

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epoxy equivalent value of about 400 to about 900 which is susceptible to ultraviolet-induced detackification.

U.S. Patent No. 4,256,828 (Smith) discloses photocopolymerizable compositions which contain
5 epoxides, organic material with hydroxyl functionality, and a photosensitive aromatic sulfonium or iodonium salt of a halogen-containing complex ion.

U.S. Patent Nos. 4,173,476 and 4,231,951 (both Smith et al.) disclose photopolymerizable epoxide
10 compositions containing triarylsulfonium complex salts as photoinitiators.

U.S. Patent No. 4,218,531 (Carlson) discloses photopolymerizable compositions containing epoxides, aromatic sulfonium complex salts, and a material
15 containing at least one non-aromatic carbon-carbon ethylenic unsaturation. The reference teaches that such compositions can be cured without generation of offensive odors.

U.S. Patent No. 4,593,051 (Koleske) discloses
20 photocopolymerizable compositions comprising an epoxide, organic compound having two or more active hydrogens per molecule, and photoinitiator.

Summary of Invention

25 The present invention provides a normally tacky, pressure-sensitive adhesive which, upon exposure to ultraviolet radiation, undergoes crosslinking to result in increased bond strength and bond durability. Bonds made with the adhesive compositions provided
30 herein typically exhibit resistance to failure, e.g., shear release, peel release, or cohesive failure, under elevated temperatures (e.g., about 100°C) and/or exposure to organic solvents. Furthermore, the compositions provided herein exhibit high transparency
35 to visible light both before and after being cured. Coupled with the bond strength characteristics mentioned above, this makes adhesive compositions of the invention well suited for use on tamper-resistant overlays for documents.

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In brief summary, the novel adhesives provided comprise, and if desired may consist essentially of, epoxide resin, polymeric film former, photoinitiator, and polyol. Adhesives of the invention may also
5 optionally contain one or more of the following: reactive diluent, solvent, toughening agent, and other additive.

Adhesives of the present invention typically exhibit an initial tackiness sufficient to provide an
10 initial peel strength of about 0.28 kilograms/centimeter-width (25 ounces/inch-width) when laminated to a stainless steel panel and rolled once with a 2.0 kilogram (4.5 pound) roller. Prior to being cured, the adhesives provide a low bond strength, i.e., an overlap
15 shear strength of less than about 7.0 kilograms/centimeter² (100 pounds/inch²) when laminated between chromic acid etched aluminum panels. Upon full cure of the adhesive with ultraviolet radiation activation, sometimes in conjunction with heat, a bond
20 strength sufficient to provide an overlap shear strength of about 141 kilograms/centimeter² (2000 pounds/inch²) on chromic acid etched aluminum may be achieved.

Detailed Description of Illustrative Embodiments

25 Epoxide resins which may be used herein include those containing two or more epoxide groups having the formula:



and which are liquid at room temperature. The polymeric
35 film formers discussed below are typically relatively non-tacky. In order to impart desired room temperature tacky, pressure-sensitive characteristics to the overall composition, the epoxide resin is preferably a liquid at room temperature. Illustrative examples of useful
40 epoxide resins include diglycidyl ethers of various phenols, e.g., bisphenol A ("DGEBA"), hydrogenated

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bisphenol A ("DGEHBA"), and bisphenol F ("DGEBF"); cycloaliphatic epoxides; epoxide cresol novolac resins; epoxide phenol novolac resins; and the like. Such epoxide resins may be used singly or in combinations of
5 two or more.

DGEBA resins are commonly available, e.g., from Shell Chemical Company, Dow Chemical Company, and Ciba Geigy Company. Typically, low molecular weight DGEBA resins with an epoxy equivalent weight of below about
10 280 are preferred. DGEBA resins with epoxy equivalent weights substantially above that range, e.g., above about 300 or more, typically tend to be more solid in character and less liquid in character at room temperature, thereby reducing the desired tackiness of
15 the composition.

Illustrative examples of cycloaliphatic epoxide resins useful herein include those having an average of two or more epoxide groups per molecule. The preferred cycloaliphatic epoxide is 3,4-epoxide cyclohexylmethyl
20 -3,4-epoxidecyclohexane carboxylate, e.g., available commercially as EPOXIDE ERL 4221 from Union Carbide Company. Readily available, this is a fast reacting, low viscosity resin. Bis(3,4-epoxidecyclo-hexylmethyl) adipate is an illustrative example of a cycloaliphatic
25 epoxide resin which is useful herein.

Phenol-novolac and cresol-novolac epoxide resins are multifunctional resins derived from epichlorohydrin and polynuclear phenolic or cresol novolac. They are typically characterized by low
30 amounts of ionic and hydrolyzable chlorine impurities and high chemical and thermal resistance. Illustrative examples of commercially available supplies thereof include Ciba-Geigy's EPN and ECN Epoxide Resin series.

Adhesive compositions of the present invention
35 may contain one or more of the epoxide resins described above. Preferably, the room temperature viscosity of the epoxide resin mixture is between about 1,000 and about 30,000 centipoise, preferably between about 3,000 and about 20,000 centipoise. Adhesive compositions made

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with epoxide resins having viscosities which are too high may tend to exhibit undesirably low tack, whereas those made with epoxide resins having viscosities which are too low may tend to be subject to resin migration and phase separation.

The polymeric film former is a polymeric material having a molecular weight which is higher than that of the epoxide resin component. The film former should be compatible with the epoxide resin, i.e., they should not undergo phase separation such as during storage of the resultant adhesive composition or of an article comprising same. Polymeric materials which can form a tough film at room temperature are preferred. The film former preferably has a weight average molecular weight between about 10,000 and about 30,000. Adhesive compositions made with film formers having molecular weights which are too low tend to provide poorer peel strength prior to photopolymerization. Adhesive compositions made with film formers having molecular weights which are too high may be harder to make as the film former is typically more difficult to handle, to dissolve, etc., and may be too viscous.

Illustrative examples of polymeric film formers which are useful herein include polyacrylates, polymethacrylates, phenoxy resins, polysulfones, and polyether sulfones.

The proportion of film former incorporated in adhesives of the invention will depend in part upon the nature of the epoxide component, the particular film former, and the degree of room temperature tackiness desired. Typically, adhesives of the invention will contain between about 15 and about 100, preferably between about 20 and about 80, and most preferably between about 40 and about 60, parts by weight of film former per 100 parts by weight of epoxide component.

Adhesive compositions of the invention typically contain a polyol component to increase the initial tackiness, post cure flexibility, and open time of the adhesive composition. Illustrative examples of

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polyols which are useful in adhesive compositions of the invention include the following: polyether polyol, polyester polyol, polycaprolactone polyol. The
5 disclose polyols which are useful in photopolymerizable epoxide compositions.

Adhesive compositions of the invention typically contain between about 2 and about 20 parts, preferably between about 3 and about 15 parts, and more
10 preferably between about 4 and about 10 parts, by weight of polyol per 100 parts by weight of epoxide component. Adhesive compositions containing too much polyol tend to undergo ultraviolet curing more slowly and, once cured, exhibit lower peel strengths. Adhesive compositions
15 containing too little polyol may not cure completely, even with thermal post treatment.

Many photoinitiators known for use in photopolymerizable epoxide compositions may be used in adhesive compositions of the invention. Illustrative
20 examples are disclosed in the aforementioned U.S. Patent Nos. 4,231,951 and 4,256,828 and U.S. Patent No. 4,058,401 (Crivello). Preferred photoinitiators include triaryl sulfonium salts and diaryl iodonium complex salts. These photoinitiators are typically thermally
25 stable and readily available commercially and exhibit good ultraviolet reactivity.

Adhesive compositions of the invention typically contain between about 1 and about 10, preferably between about 1.5 and about 6, and more
30 preferably between about 2 and about 4, parts by weight of photoinitiator per 100 parts by weight of epoxide component. Use of excessive amounts of photoinitiator may act as a screen, thereby impairing the desired photopolymerization of the adhesive. Also, large
35 residual amounts of unused initiator may tend to impair the bonding characteristics of the cured adhesive.

If desired, adhesive compositions of the invention may also contain one or more of such additives as metal particles, metal-coated particles, coloring

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agents, processing aids, adhesion promoters, wetting agents, and coupling agents.

5 Metal particles and metal-coated particles can be incorporated to render the adhesive composition conductive including anisotropically conductive if desired. Illustrative examples include nickel particles between about 6 and about 25 microns in diameter which can be randomly dispersed in the composition.

10 The adhesive composition may be substantially clear and colorless or may be colored by use of such coloring agents as dyes and pigments. It will be understood, however, that coloring agents may tend to increase the opacity of the adhesive composition so as to affect the photocuring properties thereof,
15 particularly when the adhesive is used in thick layers. Accordingly, coloring agents used herein should be selected and used in such quantities as will not undesirably inhibit the photocuring properties of the adhesive composition.

20 Adhesive compositions of the invention may contain processing aids and modifiers, e.g., rheology controlling agents such as fumed silica. Illustrative examples of adhesion promoters and coupling agents include silanes and titanates. Fluorochemical and other
25 surface energy controlling agents may be used. The various components used in compositions of the invention are preferably compatible with each other such that the cured adhesive is substantially transparent, thereby permitting the composition to be used in overlays, e.g.,
30 over information on documents.

Adhesives of the invention may be supplied in film form, e.g., between release liners as a transfer tape, to be laminated to a substrate.
Photopolymerization of the composition may be performed
35 after the various elements are assembled, e.g., by exposure to ultraviolet radiation through a substrate which is sufficiently transparent to such wavelengths, or the adhesive may be exposed prior to assembly. Under typical conditions, e.g., temperature of about 25°C,

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relative humidity of about 60 percent, and UV exposure of about 0.1 Joule/centimeter², adhesive compositions of the invention typically exhibit an open time of about 1 to 2 minutes.

5 Adhesive compositions of the invention can be used to bond substrates that previously known thermally cured epoxide adhesives bonded, simultaneously providing the advantages discussed herein. Subsequent to curing by ultraviolet radiation, adhesives of the invention may
10 optionally be heated, i.e., thermally postcured or thermal post treatment, to enhance the structural bond strength of the bond. Typically, such treatment involves heating the adhesive to a temperature of about 100°C to about 120°C for several minutes.

15 In some instances, adhesives of the invention can be used to make transparent overlays for making documents more tamper-resistant. One typical embodiment of such overlays comprises a protective cover sheet such as disclosed in U.S. Patent No. 3,170,183 (Sevelin et
20 al.), incorporated herein by reference, with a layer of the adhesive provided herein on the back side. In an inexpensive embodiment, the cover sheet may simply be single or multi-ply polymer film, e.g., polyester, which is typically preferably flexible and abrasion resistant.

25

Examples

 The invention will be further explained by the following illustrative examples which are intended to be nonlimiting. Unless otherwise indicated, all amounts
30 are expressed in parts by weight.

 Unless otherwise indicated, the following test method was used.

Overlap Shear Strength

35 Overlap Shear Strength of indicated adhesives was determined using aluminum panels having an overlap region of about 1.0 inch by about 0.5 inch (2.5 by 1.3 centimeters). The aluminum panels were conditioned in chromic acid at a temperature of about 65°C to about

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70°C for about 15 minutes and then rinsed with tap water. The panels were then allowed to dry at room temperature for about 30 minutes and then at about 60°C to about 65°C for 30 minutes. The subject adhesive was applied to a test panel at a thickness of about 1 to about 2 mils (25 to 50 microns), activated with ultraviolet radiation as indicated, and then the second panel laminated thereto. Unless otherwise indicated, the bond was then thermally postcured at about 110°C to about 115°C for 20 minutes.

Examples 1-4

Adhesives were made using the following components:

15	<u>Notation</u>	<u>Explanation</u>
	EPON 828	DGEBA resin from Shell Chemical Company;
	DER 684-EK40	Phenoxy resin in MEK, 40 percent by volume, from Dow Chemical Company;
20	UCAR PKHH	Solid phenoxy resin from Union Carbide Company;
	TASHFA	Triarylsulfonium hexafluorantimonate;
	NIAX PPG 4025	Polypropylene glycol from Union Carbide Company;
25	BTA-IIIF	Plastic toughening agent from Rohm and Haas Company;
	CABOSIL M-5	Fumed silica, surface area 200 ± 25 meters ² /gram, from Cabot Corporation;
30	CABOSIL N70-TS	Fumed silica, surface area 100 ± 20 meters ² /gram, from Cabot Corporation;
	MEK	Methyl ethyl ketone, reagent grade;
	Ni-CP	Nickel-coated particles, 10 micron average diameter.
35		

The composition in each Example was as follows:

<u>Component</u>	<u>Example</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
EPON 828	35.0	35.0	35.0	30.0

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	DER 684-EK40	21.0	0.0	24.0	36.0
	UCAR PKHH	0.0	9.0	0.0	0.0
	TASHFA	1.70	1.70	0.73	0.75
	NIAX PPG 4025	1.50	1.50	1.70	2.0
5	BTA-IIIF	4.0	0.0	0.0	0.0
	CABOSIL M-5	1.3	1.3	0.0	0.0
	CABOSIL N70-TS	0.0	0.0	1.25	1.3
	MEK	2.0	15.0	0.0	4.0
	Ni-CP	0.0	0.0	2.5	0.0

10 In Examples 1 and 2, the adhesive compositions were cured with 6 seconds exposure to a 100 watt UV-A mercury bulb providing a UV input of about 0.2 Joules/centimeter² at room temperature. In Examples 3 and 4, the adhesive compositions were cured with a 200
15 Watts/inch electrodeless mercury lamp in a UV processor. The exposure was measured with a UV-A radiometer to be about 0.050 Joules/centimeter². The joints were thermally postcured under slight compression pressure using small binder clips. In each sample, the adhesive
20 composition was substantially transparent before and after cure.

 The Overlap Shear Strength of the adhesive in each Example in kilograms/centimeter² (in pounds/inch²) was as follows:

25	Example	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
	Overlap Shear	211	120	127	127
		(3000)	(1700)	(1800)	(1800)

Example 5

30 Adhesive of the same composition as in Example 3 was placed in a thickness of between about 1.5 and about 2.0 mils (37 and 50 microns) onto two substrates: (1) a gold-plated circuit board and (2) a glass slide. The adhesive was activated with exposure to a 200
35 Watt/inch mercury lamp with total energy output of about 0.050 Joules/centimeter². A flexible printed circuit was laminated to the adhesive under about 30 kilograms/centimeter² pressure at about 110°C for 10

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seconds. The laminates were postcured at 110°C for 20 minutes.

The resistance between the flexible printed circuit leads and gold circuit board was 0.2 ohms or less. The resistance between the adjacent leads of the printed circuit was greater than 20 mega ohms, the maximum value of the ohm meter used. This demonstrates the highly anisotropic conductivity properties which may be obtained with adhesives of the invention.

10

Example 6

An adhesive was made with the following components:

	<u>Amount</u>	<u>Components</u>
15	49.3	EPONEX DRH 1510, DGEHBA epoxide resin from Shell Chemical Company;
	31.2	DER 684-EK40;
	1.7	NIAX PPG 4025;
	2.9	TASHFA;
20	14.0	MEK;
	0.9	CABOSIL M-5.

The adhesive was coated with a knife coater onto the bottom side of 3M CONFIRM Brand Retroreflective Security Laminate from which the commercially-shipped adhesive had been removed to provide a dry thickness between about 1 and about 2 mils (25 to 50 micrometers). After evaporation of the MEK solvent, several samples of the laminate were cut from the sheet and applied to a document.

Each sample was exposed through the security laminate using a 100 Watt UVA mercury bulb placed at between about 3 and about 5 inches from the document to cure the adhesive. Irradiation for between about 0.5 and about 3 minutes provided substantially equivalent performance. The text on the document was easily readable through the overlay in each sample.

Different samples were treated with high temperature, low temperature, water immersion, high humidity, and immersion in organic solvents. Even after

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treatment or immersion for the indicated periods, none of the samples could be removed from the document without so severely damaging the document or the overlay as to render them unusable. Samples were exposed to the indicated conditions or immersed in the indicated solvents for the indicated period shown in Table I. Unless otherwise indicated, test was performed at room temperature of about 23°C.

Table I

	<u>Condition</u>	<u>Duration</u>
10	Exposure to 150°C	30 minutes
	Exposure to -30°C	30 minutes
	Immersion in water at 23°C	30 days
	Exposure to 100 percent	30 days
15	relative humidity at 60°C	
	Immersion in Heptane	24 hours
	Immersion in Turpentine	24 hours
20	Immersion in Acetonitrile	1 hour*
	Immersion in Toluene	1 hour*
	Immersion in Methanol	1 hour*
	Immersion in Isopropanol	1 hour*
	Immersion in Acetone	1 minute*
25	Immersion in Dimethyl formamide	1 minute*
	Immersion in Ethyl acetate	1 minute*
	Immersion in Chloroform	1 minute*

 * Substrate was destroyed when tested for longer durations. Adhesive not observed to have degraded.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

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Claims:

1. An adhesive that is tacky at room temperature, characterized in that said adhesive comprises:

- a) at least one epoxide resin which contains two or more epoxide groups having the formula:



- b) at least one polymeric film former,
15 c) at least one photoinitiator; and
d) at least one polyol;

wherein said adhesive exhibits an increase in bond strength upon exposure to ultraviolet radiation.

20 2. The adhesive of claim 1 further characterized in at least one of the following:

- a) said epoxide resin comprises one or more of the following: diglycidyl ethers of phenol,
25 cycloaliphatic epoxides, epoxide cresol novolac resins, and epoxide phenol novolac resins; or
b) said epoxide resin is a diglycidyl ether of bisphenol A having an epoxy equivalent weight of below about 280; or
c) said epoxide resin is 3,4-epoxide
30 cyclohexymethyl-3,4-epoxidecyclo- hexane carboxylate; or
d) the room temperature viscosity of said epoxide resin component is between about 1,000 and about 30,000 centipoise.

35

3. The adhesive of claim 1 further characterized in at least one of the following:

- a) said polymeric film former has a weight average molecular weight of between about 10,000 and about
40 30,000; or

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- b) said polymeric film former comprises one or more of the following: polyacrylate, polymethacrylate, phenoxy resin, polysulfone, and polyether sulfone.

5 4. The adhesive of claim 1 further characterized in at least one of the following:

- a) said adhesive contains between about 15 and about 100 parts by weight of film former per 100 parts by weight of epoxide component; or
10 b) said adhesive contains between about 20 and about 80 parts by weight of film former per 100 parts by weight of epoxide component; or
c) said adhesive contains between about 40 and about 60 parts by weight of film former per 100 parts by
15 weight of epoxide component.

 5. The adhesive of claim 1 further characterized in at least one of the following:

- a) said polyol component includes one or more of the
20 following: polyether polyol, polyester polyol, polycaprolactone polyol.
b) said adhesive contains between about 2 and about 20 parts by weight of polyol per 100 parts by weight of epoxide component.
25 c) said adhesive contains between about 3 and about 15 parts by weight of polyol per 100 parts by weight of epoxide component; or
d) said adhesive contains between about 4 and about 10 parts by weight of polyol per 100 parts by
30 weight of epoxide component.

 6. The adhesive of claim 1 further characterized in at least one of the following:

- a) said photoinitiator component contains one or more
35 of the following: triaryl sulfonium salts and diaryl iodonium complex salts; or
b) said adhesive contains between about 1 and about 10 parts by weight of photoinitiator per 100 parts by weight of epoxide component; or

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- c) said adhesive contains between about 1.5 and about 6 parts by weight of photoinitiator per 100 parts by weight of epoxide component; or
- d) said adhesive contains between about 2 and about 4 parts by weight of photoinitiator per 100 parts by weight of epoxide component.

7. The adhesive of claim 1 characterized in that said adhesive further comprises one or more of the following: metal particles, metal-coated particles, coloring agents, processing aids, adhesion promoters, wetting agents, and coupling agents.

8. A transparent overlay comprising a protective cover sheet and a layer of the adhesive of claim 1 on one side thereof.

INTERNATIONAL SEARCH REPORT

PCT/US 92/01974

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C09J163/00; C08G59/68		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09J ; C08F ; C08G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 690 957 (FUJIOKA H. ET AL) 1 September 1987 see claims 1,2 see column 2, line 58 - line 60 see column 4, line 7 - line 13 see column 5, line 25 - line 30 ---	1-7
X	CHEMICAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL Section Ch, Week 8519, 3 July 1985 Derwent Publications Ltd., London, GB; Class A, AN 85-113545/19 & JP,A,60 055 069 (MITSUBISHI ELECTRIC CORP.) 29 March 1985 see abstract --- -/-	1-7
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
09 SEPTEMBER 1992	16. 09. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	O'SULLIVAN T.P.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claims No.
X	CHEMICAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL Section Ch, Week 8518, 26 June 1985 Derwent Publications Ltd., London, GB; Class A, AN 85-107731/18 & JP,A,60 051 717 (MITSUBISHI ELECTRIC CORP) 23 March 1985 see abstract	1,3-6
A	--- EP,A,0 227 002 (KOLLMORGEN TECHNOLOGIES CORP.) 1 July 1987 see claims 1,12,13 see example 1 see page 7, line 55 - line 57	1-7
A	--- GB,A,2 119 810 (GRACE W.R. AND CO.) 23 November 1983 see claims 1,7	1-7
A	--- WO,A,9 102 038 (H.B. FULLER CO.) 21 February 1991 see claims 1,5,8,10	1-3
A	--- EP,A,0 124 057 (DESOTO INC.) 7 November 1984 see claims 1,3 see page 4, line 1 - line 15	1,5,6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9201974
SA 60485

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4690957	01-09-87	None	
EP-A-0227002	01-07-87	AU-B- 587097	03-08-89
		AU-A- 6664686	25-06-87
		DE-A, C 3643660	25-06-87
		FR-A, B 2594838	28-08-87
		GB-A, B 2184728	01-07-87
		JP-A- 2187486	23-07-90
		JP-B- 3007709	04-02-91
		JP-C- 1590537	30-11-90
		JP-B- 2012995	03-04-90
		JP-A- 62148584	02-07-87
GB-A-2119810	23-11-83	CA-A- 1194637	01-10-85
		DE-A- 3314896	27-10-83
		FR-A- 2525611	28-10-83
		US-A- 4605465	12-08-86
WO-A-9102038	21-02-91	EP-A- 0485508	20-05-92
EP-A-0124057	07-11-84	US-A- 4585534	29-04-86
		CA-A- 1212796	14-10-86
		JP-B- 3036046	30-05-91
		JP-A- 59202264	16-11-84
		JP-A- 3184008	12-08-91